

AMENDED SPECIFICATION

[0004] The inventor has developed technology for dissociating compounds in a thermoelectric reactor using ultra-pyrolysis techniques with thermal radiation enhancement, non-equilibrium reactions derived from electromagnetic forces, and energy trapping to achieve and maintain temperatures sufficient to achieve very high conversion rates. When the compound contains hydrogen, such as hydrocarbon fuels and hydrogen sulfide, its dissociation produces hydrogen. The inventor has taught the use of thermoelectric reactors to destroy volatile organic compounds in U.S. Patent No. 5,614,156, to dissociate hydrogen sulfide into hydrogen and sulfur in U.S. Patent No. 5,843,395, and to reform hydrocarbon fuels to produce hydrogen in ~~co-pending~~ U.S. Application Serial No. 10/121,390 now abandoned.

[0006] Table 1.

Fuel	Electricity Consumption ^{¶(1)} , %	Fuel Conv. Eff. ^{¶(2)} , %	H ₂ Conv Eff. ^{¶(3)} , %	Energy Eff. ^{¶(4)} , %	H ₂ Conc. ^{¶(5)} (dry) %
Methanol	<3	~100	93-95	~100	64
Ethanol	<6	~100	94	~100	54
Gasoline	<6	~100	97	~100	65

Note: ^{¶(1)} Electric power input = % of power output (H₂) Electricity Consumption = (electrical power input)/(electrical power input + LHV of input fuel)

^{¶(2)} Fuel Conversion Efficiency = 1 - (fuel in reformat)/(input fuel)

^{¶(3)} H₂ Conversion Efficiency = (H₂ measured in reformat)/(H₂ theoretical value in equilibrium)

^{¶(4)} Energy Efficiency = (LHV of H₂ in reformat)/(LHV of input fuel + electric power input)

^{¶(5)} Measured H₂ concentration in reformat as dry basis. This concentration was measured right after the H₂ reformer (without any other gas conditioning).

LHV = Low Heating Value

[0007] The U.S. Department of Energy (USDOE), (Hydrogen Production and Delivery Research Solicitation No. DE-PS36-03GO93007, July 24, 24, 2003, pages 2, c-7)¹ estimates that currently it costs between \$5.00 and \$6.00 to produce a kilogram of hydrogen,

1 and that this cost should be reduced to \$1.50/kg to be competitive with conventional fuels.
2 The USDOE has also set a primary energy efficiency of 75% to be met in the year 2010.
3 The primary energy efficiency of conventional reformer technology for producing hydrogen
4 currently ranges up to 70%. Thus a three to four-fold decrease in cost is necessary for
5 hydrogen to become a competitively priced fuel. A significant fraction of the cost of
6 hydrogen production is the cost of the hydrocarbon fuels that are reformed. If H₂O were to
7 replace hydrocarbon fuels as the primary source of hydrogen in a reformer, such cost
8 reductions are feasible.

9
10 [0009] The present invention is a reformer that dissociates a gaseous
11 H₂O/hydrocarbon fuel input mixture in a non-equilibrium thermal plasma environment. The
12 heart of the reformer is a reaction chamber. The outer lateral wall of the reactor is an
13 emitter electrode and the inner lateral wall is a collector electrode, the emitter electrode and
14 the collector electrode forming an electric circuit. The emitter electrode contains a
15 multiplicity of thin needle-like extrusions. External electricity causes electrons to be
16 emitted copiously from the needle-like extrusions. Spindt (A Thin-Film Field Emission
17 Cathode, J. Of Applied Physics, 39, 1968, pp. 3504-3505)² discusses how these could be
18 produced. These high energy electrons are absorbed by hydrocarbon molecules and ionize
19 the hydrocarbon molecules to create a greater number of lower energy electrons than were
20 absorbed. These lower energy electrons in turn interact with H₂O to dissociate it. A non-
21 combustion pyrolysis process is used to create and maintain this environment. Dissociation
22 of H₂O is induced by ionization in the plasma environment. The present invention in part
23 replaces hydrocarbon fuels, which have costs, with H₂O, which is virtually without cost, as a
24 fuel for producing hydrogen. Preliminary cost estimates based on H₂O replacing 50% of the
25 hydrocarbon fuel and a nearly 100% primary energy efficiency indicate that a cost of less
26 than \$2.00/kg of hydrogen can be achieved. This cost can be further reduced through
27 optimization of the system and operational conditions so that the cost target of \$1.50/kg of
28 hydrogen is feasible. Therefore, an object of the invention is to reduce the cost of producing
29 hydrogen to commercially competitive levels while reducing the consumption of
30 hydrocarbon fuels. Other objects that result from reduced use of hydrocarbon fuels are

1 reducing the production of greenhouse gases and if the hydrocarbon fuels are fossil fuels,
2 reducing the use of scarce or imported fuels.

3
4 [0011] Reforming techniques that use catalysts require large reaction areas. This
5 large-area requirement imposes scalability problems and limits the quantity of hydrogen that
6 can be produced at locations with limited space such as refueling stations in a city. Since
7 this invention does not use catalysts, another object is to provide a scalable and high-power
8 density reformer for hydrogen production. The presence of H_2O results ~~[[causes]]~~ in
9 chemical reactions wherein carbon dioxide rather than carbon or soot is formed. Therefore
10 another object of the invention is to avoid carbon or soot formation.

11
12 [0015] With reference to FIG. 1 the plasma reformer, has an inlet 33 to admit a flow
13 of a gaseous mixture of H_2O and hydrocarbon fuel into the plasma reformer. This mixture
14 is preheated to a temperature in the range of $350^{\circ}C$ to $500^{\circ}C$ external to the reformer and
15 then further heated and mixed in turbulent heating zone 35. The mixture then enters
16 reaction chamber 45. The reaction chamber contains one or more emitter electrodes 10 and
17 one or more collector electrodes 20. ~~These electrodes form~~ Each emitter electrode -
18 collector electrode pair forms an electric circuit and ~~[[are]]~~ is at high temperature being
19 heated by an external supplemental source of electricity. The electrical energy produces
20 active energetic electrons ($_{hard}e^{-}$), and maintains and controls optimal plasma conditions.
21 These hard electrons produce excited species ions, free radicals, and additional lower energy
22 electrons ($_{soft}e^{-}$) through electron-impaction or electron-expelling dissociation, excitation,
23 and ionization of hydrocarbon molecules. ~~There could be a single emitter electrode or~~
24 ~~multiple emitter electrodes.~~ When multiple electrodes are used there could be in circuits
25 using different external sources of electricity, such as 110 volt AC, 220 volt AC or DC. The
26 emitter ~~electrode(s)~~ electrodes 10 are embedded in~~[[,]]~~ the outer lateral walls of the reaction
27 chamber. The collector ~~electrode(s)~~ electrodes 20, which can be single or multiple, form or
28 are embedded in the inner lateral wall of the reaction chamber, which surrounds the center
29 line C_L of the reformer. It is preferred that a filter 15, which could be made of a
30 semiconductor, such as silicon-based zirconium oxide, or a ceramic alloy such as alumina,

surrounds the collector ~~electrode(s)~~ electrodes. The filter acts to neutralize ions and to allow passing of electrons to the collector electrode(s) while slowing them down so that they impart less kinetic energy (heat) to the collector ~~electrode(s)~~ electrodes.^{[[.]]} The filter also acts as a thermal radiation shield to cool the collector electrode(s) to improve their effectiveness. The hot emitter ~~electrode(s)~~ electrodes emit active high-energy electrons (e^-_{hard}) that may be absorbed by hydrocarbon molecules in the reaction chamber or may expel orbital electrons from the hydrocarbon molecules if the energy transferred to the molecule exceeds the ionization potential of the molecule. When an orbital electron is expelled, the molecule becomes ionized and the incident or expelled electron loses energy and becomes a lower energy or soft electron (e^-_{soft}). The energy-degraded incident electron and the expelled electrons are soft electrons. More than one orbital electron can be expelled as shown in Eq. 1, where M represents a molecule

[0017] H_2O has a high ionization potential (12.6eV)^{[[2]]} and is a small molecule that presents a small target for hard electrons. Hydrocarbons are larger molecules and those that have a lower ionization potential than water are more readily ionized by hard electrons. FIG. 2 shows that the ionization potential of hydrocarbon decreases as the number of carbon atoms in the molecule, the carbon number, increases (Lias, Sharon G., Ionization Energies of Gas Phase Molecules, CRC Handbook Chemistry and Physics, 83rd Ed., pages 10-181 to 10-198)³. Ionization originates with ionization of hydrocarbons near the surface of the emitter electrodes 10. These red-hot electrodes also originate an electricity-conducting gas medium that propagates from the emitter electrodes to the collector electrodes 20. The hydrocarbon fuel in addition to being dissociated itself, by being initially ionized initiates plasma conditions that have a field of soft electrons. The soft electrons thus produced readily interact with and are absorbed by the superheated H_2O steam molecules that are energetic at the high temperatures in the reaction chamber. Soft electrons with energies about 5 eV to 6 eV are optimum for dissociating H_2O , into hydrogen and oxygen through electron impaction or absorption. Hard electrons with energy above 7 eV and ions play key roles in dissociating and ionizing hydrocarbon fuels. For hydrogen production, the preferred temperature range in the chamber is 700°C to 1000°C, although the temperature could range

1 from 400°C upwards to 1900°C. As shown in Eq. 2, steam interacts with soft electrons to
2 form ionized H₂O, or hydro-radicals, which dissociates into hydrogen and oxygen. The
3 oxygen thus produced reacts with carbon from dissociation of the hydrocarbon fuel to form
4 carbon oxides, CO_x, instead of forming carbon or coke.

5
6 **[0023]** The high-temperature fiber blankets **30** and vacuum form fibers **29** are
7 typically ceramic fibers, which may be composed of commercially-available alumina, silica,
8 or mullite. These materials have very low thermal conductivities (of the order of 0.04
9 watts/meter- °C) and are capable of withstanding high temperature (up to at least 1900 °C).
10 The compression-expansion cushion mat **40** provides thermal expansion cushion as well as
11 cushioning for vibration and shocks[[:]], seals the contact between the reformer's outer steel
12 casing **31** and the internals including the insulators **29** and **30**[[:]] and the ceramic outer wall
13 **28**[[:]], provides thermal insulation[[:]], and maintains the system durability throughout the
14 life cycle of the reformer. The compression-expansion mat **40** is made of a low thermal
15 conductivity material that has a great capability for absorbing thermal compression-
16 expansion, shocks, and vibrations, and having the capability of sealing and protecting
17 reformer internals. A commercially available mat product consisting of three basic raw
18 material (ceramic fibers, unexpanded vermiculite, and organic binder) is an appropriate
19 material for the compression-expansion mat. The ceramic walls **26** and **28** may be
20 zirconium oxide, silicon carbide or graphite. The energy retaining zone **27** and turbulent
21 heating zone **35** contain layers of heat-retaining micro-porous articulated ceramic fibers,
22 such as alumina, silica, mullite, titanate, spinel, zirconia, or some combination thereof. The
23 physical properties of these ceramic fibers (such as thermal emissivity, absorptivity,
24 reflectivity, conductivity, porosity) have some impact on energy efficiency and may
25 increase or decrease energy efficiency by as much as approximately 10 percent. The choice
26 of ceramic fibers can be optimized for specific feed streams by considering the conductive,
27 convective, and radiative heat transfer in a porous medium reactive flow for different types
28 of ceramic fibers.